Hydrogen generation by tin corrosion in lactic acid solution promoted by sodium perchlorate
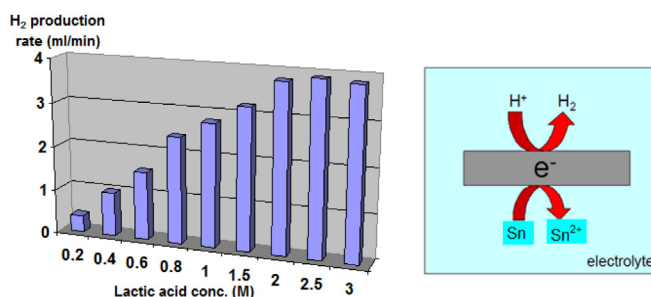
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HIGHLIGHTS

- Production of hydrogen has been achieved using the reaction of tin with lactic acid.
- The rate of hydrogen production increases with increasing lactic acid concentration.
- The presence of perchlorate ion in lactic acid promoting the hydrogen generation rate.
- Perchlorate ion disrupt the development of a coherent and adherent SnO_2 layer.
- An increase in temperature accelerates the rate of solubility of passive layer.

GRAPHICAL ABSTRACT

ABSTRACT

A method to produce high purity hydrogen using the corrosion of tin metal in lactic acid solutions is studied. The addition of sodium perchlorate has been also investigated for promoting the tin-lactic acid reaction. The data reveal that the rate of hydrogen production increases with increasing lactic acid concentration. The presence of perchlorate ions in lactic acid solution enhances the active dissolution of tin metal and tends to breakdown the passive film and promoting the hydrogen generation rate. Polarization measurements show that the breakdown potential (E_{pit}) decreases with increase in sodium perchlorate concentration. An increase in temperature accelerates the rate of solubility of passive layer on the tin surface. Moreover, a synergistic effect of sodium perchlorate in combination with increasing the solution temperature is key in promoting the hydrogen generation rate. Results obtained from hydrogen and polarization measurements are in good agreement. These measurements are complemented with SEM, EDX and XRD examinations of the electrode surface.

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1. Introduction

Due to fossil fuel depletion and air pollution arising from its combustion, there is an urgent demand for renewable, clean fuel alternatives for our future energy supply. Hydrogen, a regenerative and environmentally friendly fuel with high calorific value, has attracted much attention by scientists [1–4]. Hydrogen-based fuel cells are promising systems for future H$_2$-propelled vehicles, stationary and mobile applications [5]. Nonetheless, attractive methods for hydrogen production and storage are needed to fulfill these expectations. The development of alternative technologies for hydrogen production not based on fossil fuels is an option to

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provide clean and secure energy and to reduce CO_2 emissions [6]. In the last ten years, chemical hydrides such as NaBH4 [7], LiBH$_4$, NaAlH$_4$ and NH$_3$BH$_3$ [8—10] have received much attention as on-board hydrogen production materials due to their high hydrogen production density. However, their high cost has been a limiting factor for commercial applications. Recently, the on-board hydrogen production method involving the hydrolysis of electro-chemically active metals, such as Al, Mg, Zn [11—13], have been studied by many researchers because they are more economical compared with chemical hydrides.

Generation of hydrogen for fuel cells by reaction of corrosion of metal with water or aqueous solutions reduces storage weight and/ or volume over high pressure or cryogenic storage.

Corrosion is a process that involves electrochemical as well as chemical reactions [14]. The electrochemical reactions differ from the chemical reactions in that an exchange of electrons occurs at the interface between the metal and the solution [15]. In order to maintain a balance of charge, two reactions occur at the surface. The metal dissolution reaction, or anodic reaction, results in the loss of electrons, while the coupled cathodic reaction results in a species gaining electrons. An example of these two reactions is shown in Equations (1) and (2), where metal is being oxidized to ions while hydrogen ions are being reduced such that hydrogen is evolved [16].

$$M \rightarrow M^{n+} + ne \qquad (1)$$

$$2H^+ + 2e \rightarrow H_2 \qquad (2)$$

The hydrolysis of aluminum metal has the potential to generate hydrogen directly from water [17]. However, the principal disad-vantage of using aluminum as a hydrogen-generating material is highly inert of aluminum in water because of an alumina film on its surface, which prevents the reaction between aluminum and water. This alumina film would generally not allow reaction (1) or (2) to take place to produce hydrogen.

The alternative idea of using the corrosion reaction of tin metal with lactic acid solution for the production of hydrogen has been evaluate in the present study. Actually, tin metal is easy to be corroded in organic acid to produce hydrogen. On the other hand, tin is stable under usual conditions and much less expensive than chemical hydrides: the price of tin (23 \$ kg^{-1}) is 20 times lower than the price of sodium borohydride (460 \$ kg^{-1} [18,19]. In addi-tion, hydrogen generation from tin in acid solution can be achieved under mild conditions of temperature and pressure. Nevertheless, data regarding the use of the hydrolysis of tin metal in lactic acid for hydrogen production appears to be very poor.

A number of reaction-promoting approaches have been also investigated for the tin-lactic acid reaction. This includes addition of sodium perchlorate and an increase in solution temperature.

2. Experimental

2.1. Preparation of materials

The working specimens employed in the present work was made of spec pure tin (99.998% purity). Before being used, speci-mens were mechanically polished with emery paper up to 600 grit, rinsed with distilled water, alcohol and acetone and dried.

The specimens for the hydrogen generation test were prepared by cutting the bulk form into $2 \times 2 \times 1$ cm^3 samples. The exposed surface area of all of the specimens was kept constant at 16 cm^2.

For polarization measurements, the investigated specimens were cut as cylindrical rods, welded with Cu—wire for electrical connection and mounted in glass tubes of appropriate diameter using Araldite to offer an active flat disc shaped surface of (0.50 cm^2) geometric area, to contact the test solution.

Lactic acid (Merck) of AR grade was used for preparing solutions. Sodium perchlorate (98% purity) was supplied by Sigma—Aldrich.

All reagents were used as received. Distilled water was used to prepare the aqueous solutions. The different solutions tested in this study were freshly prepared before performing the experiments.

The solution temperature was adjusted to within $\pm 0.2\ ^\circ$C using a water thermostat.

2.2. Measurement of the hydrogen generation rate

The equipment used in the hydrogen generation experiments has been described in a previous work [16]. In monitoring corrosion studies using this technique, the volume of hydrogen gas evolved from the corrosion reaction of tin specimens in 100 ml of lactic acid solutions was monitored by volume changes in the level of paraffin oil in the graduated burette at fixed time intervals. Each experiment was repeated three times to ensure reproducibility, and the average values are reported.

2.3. Polarization measurements

For polarization measurements, a conventional three-electrode glass cell with a platinum counter electrode, a saturated calomel electrode (SCE) as reference and tin metal as the working electrode was used. The potentiodynamic current—potential curves were recorded using a potentioscan type (Potentiostat/Galvanostat EG&G model 273) connected with a personal computer. The potentiodynamic E/j were carried out by changing linearly the electrode potential automatically from the starting potential (-2.0 V versus SCE) towards more positive direction with a required scan rate till the end of the experiment.

2.4. Surface analysis

Surface morphology of tin samples was examined after the desired tests by employing scan electron microscopy (SEM). The SEM studies were carried out using JOEL-JEM-1200 EX II ELETRON MICROSCOPE.

Energy dispersive X-ray spectroscopy (EDS) investigations were carried out in order to identify the elemental composition of the species formed on the metal surface after the desired tests. The EDX studies were carried out using a Traktor TN-2000 energy dispersive spectrometer.

The composition of the corrosion products formed on the electrode surface was examined by X-Ray diffraction XRD analysis (model: philips p.w. /NO. 1730).

3. Results and discussion

3.1. Effect of lactic acid concentration

Fig. 1 shows the hydrogen generation rate from the reaction of tin metal and lactic acid at 25 °C. It is observed that there is a rapid increase in the hydrogen generation rate with increase in the concentration of lactic acid till it reaches a maximum at 2.5 M, indicating acceleration behavior for the tin dissolution. Any further increase in the concentration of lactic acid results in a slightly decrease in the hydrogen generation rate. This can be due to the decrease in the degree of lactic acid dissociation at high acid concentration.

The dissolution of two valence metal more electronegative than hydrogen (in this case it is tin), in lactic acid solution, represents the complex reaction consisting of several degrees, some developing
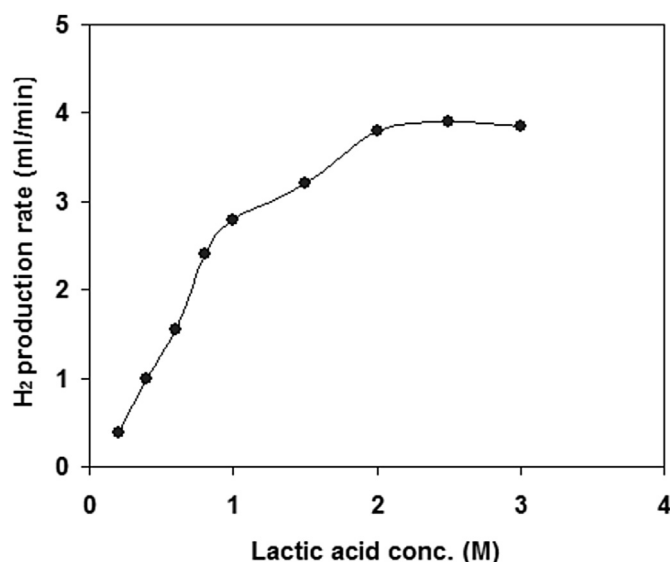
Fig. 1. Hydrogen production rate from corrosion of tin in various lactic acid solution concentrations at 25 °C.

Fig. 2. Hydrogen production rate from corrosion of tin in 1.0 M lactic acid solution at various sodium perchlorate concentrations at 25 °C.

successively and some simultaneously. Having in mind that the process of metal dissolution is followed by hydrogen evolution (the reduction of hydrogen ion), this process can be treated as tin corrosion with hydrogen evolution [20]. The reaction of tin dissolution in lactic acid solution can be represented by the equation [21]:

$$Sn + 2H^+ \rightarrow Sn^{2+} + H_2 \qquad (3)$$

During the last decades, it has been well established that the hydrogen production occurs via two successive elementary events [22,23]:

The initial discharge of hydrogen ions to adsorbed monoatomic hydrogen.

$$H^+ + e \rightarrow H^{\bullet} \qquad (4)$$

Followed by the chemical (Equation (5)) or electrochemical (Equation (6)) recombination of monoatomic hydrogen to molecular hydrogen.

$$2H^{\bullet} \rightarrow H_2 \qquad (5)$$

$$H^+ + H^{\bullet} + e \rightarrow H_2 \qquad (6)$$

3.2. Effect of sodium perchlorate as hydrogen generation promoter

A systematic study was performed in order to determine the effect of sodium perchlorate concentration on the hydrogen generation from the reaction of tin metal and 1.0 M lactic acid at 25 °C. So, a series of experiments were carried out covering a range of concentrations between 0.05 and 0.5 M. The effect of sodium perchlorate concentration on hydrogen production rate is shown in Fig. 2. It is clear that the hydrogen generation rate during the corrosion reaction of tin with 1.0 M lactic acid solution was found to increase in the presence of sodium perchlorate compared to its absence (blank). This is an indication that sodium perchlorate has been employed to promote tin-lactic acid hydrogen production reactions. An increase of sodium perchlorate concentration caused a raise in the hydrogen generation rate as can be observed in Fig. 2.
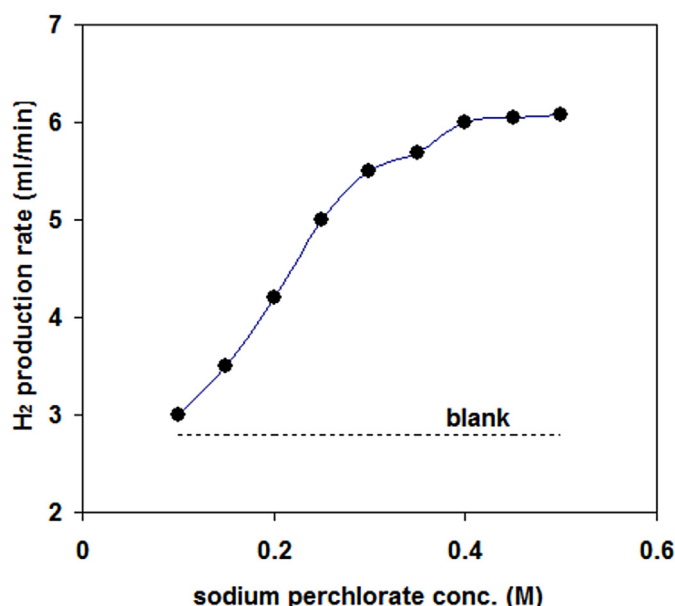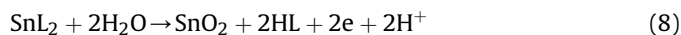
The promoter effect of sodium perchlorate can be explained on the basis that the dissolution of tin in lactic acid (HL) is accompanied by the following reactions [24]:

$$Sn^{+2} + 2HL \rightarrow SnL_2 + 2H^+ \qquad (7)$$

$$SnL_2 + 2H_2O \rightarrow SnO_2 + 2HL + 2e + 2H^+ \qquad (8)$$

Dissolved ion of Sn^{2+} in lactic acid formed a complex of Sn (II) − lactate (SnL_2). The complex (SnL_2) adsorbed on the surface of tin was oxidized to SnO_2. Although these reactions is thermodynamically favorable, it does not proceed due to the presence of a coherent and adherent layer of SnO_2 which forms on the surface of tin metal which prevents water and SnL_2 from coming into direct contact with the tin metal. The key to inducing and maintaining the reaction of tin with lactic acid is the continual removal and/or disruption of this coherent/adherent SnO_2 layer. The addition of sodium perchlorate can produce localized pitting and rupture of the SnO_2 layer on tin metal. Such effects have been employed to promote tin-lactic acid hydrogen production reactions [25]. Breakdown of the passive layer and initiation of pitting attack can be ascribed to competitive adsorption between ClO_4^- and oxygenated species at adsorption sites on oxide covered layer. The adsorbed ClO_4^- ions can penetrate through passive layer especially at its defect points and flaws with the assistance of a high electric filed to reach the base metal surface. Following this, pit growth occurs sooner as a result of increasing the concentration of ClO_4^- results form its migration and increasing the acidity as a result of hydrolysis of metal cations inside pits [26].

3.3. Combined temperature and sodium perchlorate promoters

In this section we study the effect of temperature on the hydrogen generation from the reaction of tin metal and 1.0 M lactic acid solution in the presence of 0.5 M sodium perchlorate. The data is shown in Fig. 3. Prior to starting the experiments, tested solutions (1.0 M lactic acid + 0.5 M sodium perchlorate) were initially heated to selected temperatures between 25 and 90 °C. Once the temperature was equilibrated, the experiment was fulfilled by
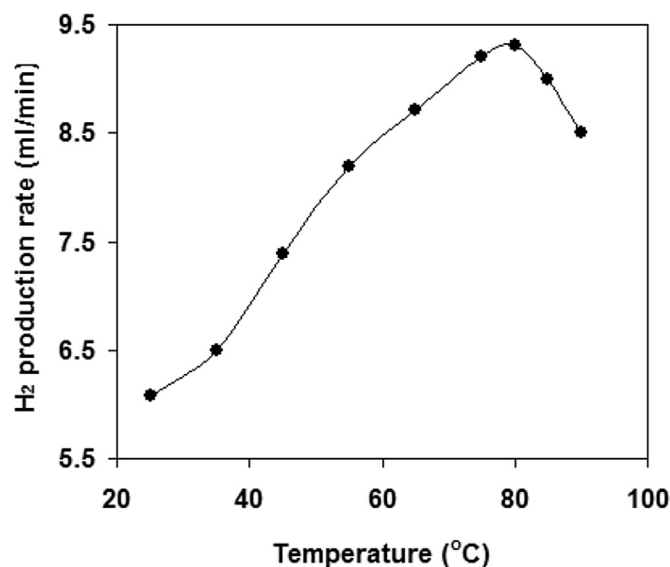
Fig. 3. The effect of solution temperature on the hydrogen production rate from corrosion of tin in 1.0 M lactic acid solution containing 0.5 M sodium perchlorate.

dropping tin metal to the preheated tested solutions. It is clear that the hydrogen generation rate increases with the rise of temperature till it reaches a maximum at 80 °C. Such effect of temperature on promoting the hydrogen generation rate may be attributed to an increase in solubility of oxide film (SnO_2) with temperature. In addition, an increase in temperature accelerates the rates of diffusion and migration of the reactant and product species [27]. Consequently, the rise of temperature aids sodium perchlorate in producing localized pitting and rupture of the SnO_2 layer on tin metal.
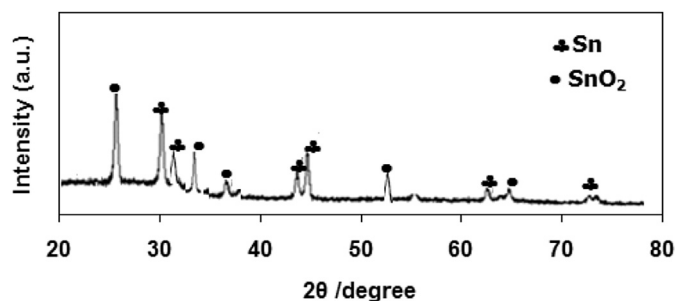

Fig. 5. XRD pattern for corroded surface of tin in 1.0 M lactic acid solution 25 °C.

The data clearly show also that any further increase in solution temperature (more than 80 °C) result in a decrease in the hydrogen generation rate. This behavior may be due to the decrease in oxygen solubility in aqueous solutions with the increase in temperature until at the boiling point all oxygen is removed; this factor tends to decrease the corrosion rate.

3.4. Polarization study

Fig. 4 illustrates the potentiodynamic polarization curves recorded for tin in lactic acid solutions (0.2–1.0 M) between −2.0 and 2.0 V (SCE) at a scan rate of 0.5 mV s^{-1} and at 25 °C.

The potentiodynamic polarization technique is generally used to produce a qualitative picture or "fingerprint" of a substance in a given solution [28]. It also detects important information such as: the potential region over which the specimen remains passive, the corrosion rate in the passive region and the ability of the material to spontaneously passivate in the particular medium. Region "A" in Fig. 4 is the region in which the hydrogen reduction and evolution of hydrogen gas occur. On positive going sweep, the cathodic current decreases continually and changes its sign at corrosion potential. Region "B" in Fig. 4 is the region in which tin metal
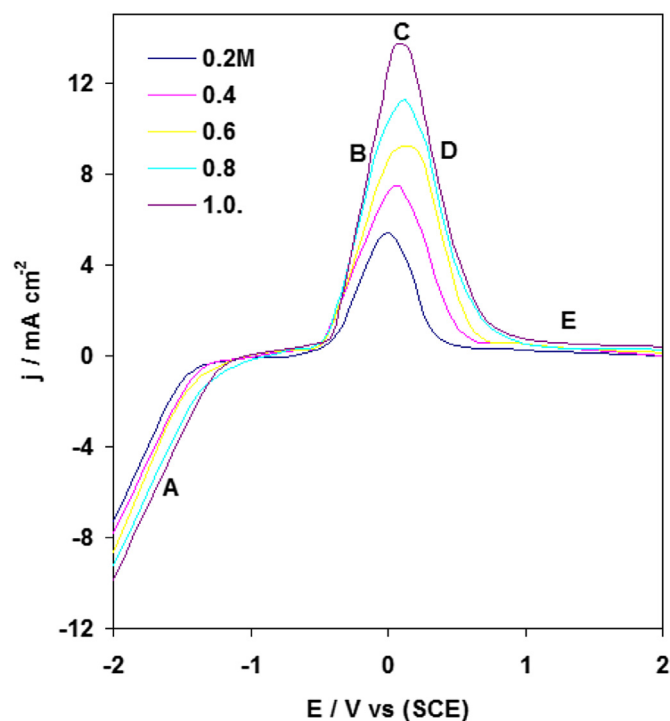

Fig. 4. The potentiodynamic polarization curves for tin in various lactic acid solution concentrations at 25 °C.
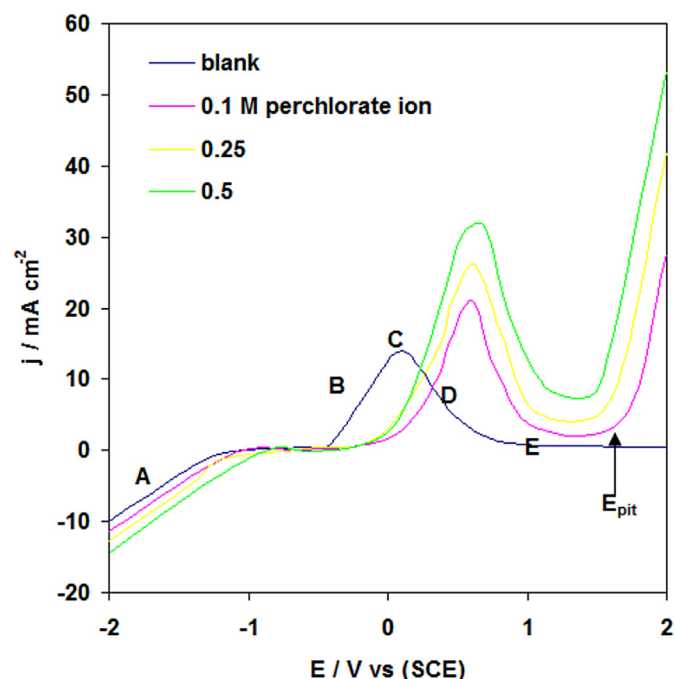

Fig. 6. The potentiodynamic polarization curves for tin in 1.0 M lactic acid solution in the absence and presence of different concentrations of sodium perchlorate at 25 °C.
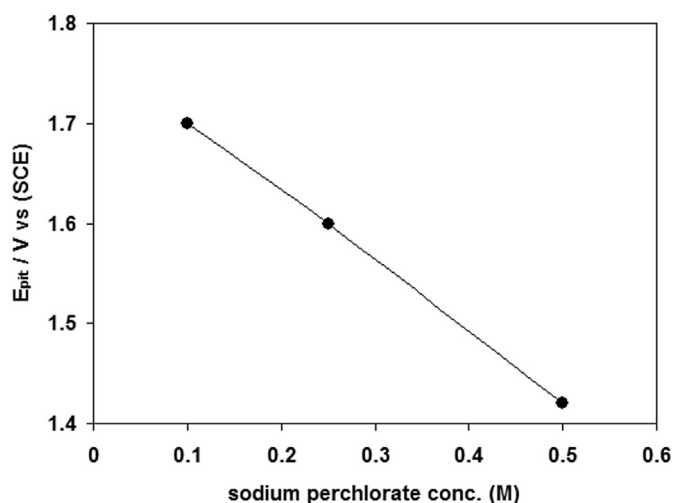
Fig. 7. Relation between E_{pit} versus sodium perchlorate concentrations.

specimen corrodes, as the applied potential is made more positive. At "C" the onset of passivation begins. The passivation begins. The passivation is probable due to the formation of SnO_2 on the surface of the metal. This point is characterized by two values, the primary passive potential (E_{pp}) and the critical current density (j_c). In region D, the current decreases rapidly as the passivating film forms on the specimen. In region E, represents the passive region. It clear from Fig. 4 (region A) that at any polarization potential between −2.0 and −1.4 V, the cathodic current increases with increasing lactic acid concentration. The current is related by Faraday's law to the quantity of the species that is being generated [29]; therefore, an increase in the lactic acid concentration causes an increase in the production rate of hydrogen gas. It is clear also that critical current density j_c of anodic peak enhances with increasing the acid concentration. This is usually indicative of increasing corrosion rate of tin with increasing acid concentration.

XRD analysis (Fig. 5) was performed to verify the compositions of corrosion products on tin surface. It is observed that the main oxide that formed on the metal surface is SnO_2.

Fig. 6 represents typical potentiodynamic polarization responses of tin metal in solution containing 1.0 M lactic acid without (blank) and with different concentration of sodium perchlorate at a scan rate of 0.5 mV s^{-1} and at 25 °C. The data reveal that in the absence of sodium perchlorate (blank), the passive region extends up to 2.0 V with almost constant current density (j_{pass}) without exhibiting a critical breakdown potential or showing any evidence of pitting attack. On other hand, the polarization curves exhibit remarkable changes in the passive region after addition of sodium perchlorate. When a certain critical potential (E_{pit}) is reached, the passive current density (j_{pass}) begins to rise suddenly without any sign for oxygen evolution, indication passivity breakdown and initiation of pitting attack. Once a pit is nucleated, pitting growth is believed to proceed in the active dissolution mode. Initiation of pitting attack could be ascribed to adsorption of perchlorate ions on the oxide/solution interface under the influence of electric field (at the oxide/solution interface) in competition with the oxygenated species for surface sites on the hydrated oxide [30]. The adsorption process is followed by chemical reaction between the adsorbed perchlorate ions and tin oxide cations on the hydrated oxide surface. These processes lead to the formation of $Sn(OH)_2(ClO_4)^-$ complexes [31]. The soluble complexes immediately separate from the oxide lattice and readily go in solution [32]. The process of localized dissolution of the oxide film via the formation of soluble species continues until the passive film locally dissolves. Once the passive film is locally dissolved, pit nucleates at the critical breakdown potential E_{pit} and dissolution of the substrate metal begins. The preferential sites for $(ClO_4)^-$ adsorption are likely to be areas of oxide surface defects and films where the oxide thickness is smaller than in adjacent areas, and therefore the assistant electric field across the oxide/solution interface is higher [32]. The pit growth and the sudden rise in anodic current occur as a result of an increase in the $(ClO_4)^-$ ion concentration, resulting from its migration and a decrease in the pH as a result of hydrolysis of Sn^{2+} ions at the incipient pits. Inspections of the data obtained display that the breakdown potential E_{pit} depends considerably on the concentration of $(ClO_4)^-$ ions, where an increase in $(ClO_4)^-$ concentration shifts E_{pit} towards more negative (active) direction corresponding to decreased resistance to pitting corrosion (see Fig. 7). This result supports the assertion that the addition of sodium perchlorate employed to promote tin-lactic acid hydrogen production reactions. This clearly shown from Fig. 6 (region A) that at any polarization potential between −2.0 and −1.4 V, the cathodic current increases with increasing sodium perchlorate concentration.

3.5. SEM/EDX examination

The surface morphologies of tin electrode after 6 h immersions in 1.0 M lactic acid solution in the absence and presence of 0.5 M of sodium perchlorate at 25 °C are presented in Fig. 8.

Fig. 8a shows the blank material of tin electrode before immersion in test solutions; microstructure displayed the presence of a uniform finishing produced by the mechanical grinding on the sample. Fig. 8b shows a general view of surface sample after immersions in 1.0 M lactic acid solution, the formation of a dense film of corrosion products is observed on the metal surface. In the presence of 0.5 M of sodium perchlorate in 1.0 M lactic acid solution
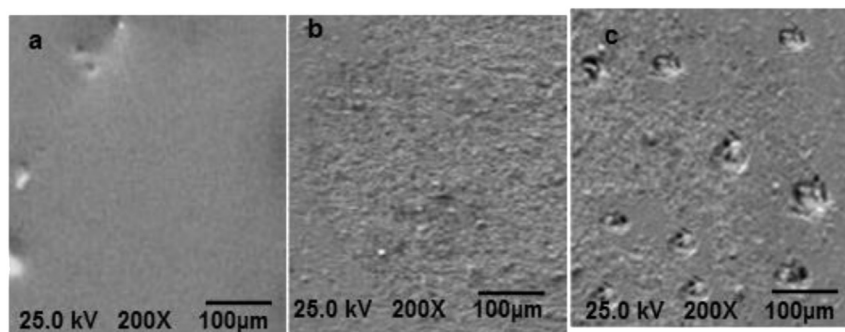

Fig. 8. SEM images recorded for a polished tin sample (image a), tin sample corroded in 1.0 M lactic acid solution (image b) and tin sample corroded in 1.0 M lactic acid solution containing 0.5 M sodium perchlorate (image c).
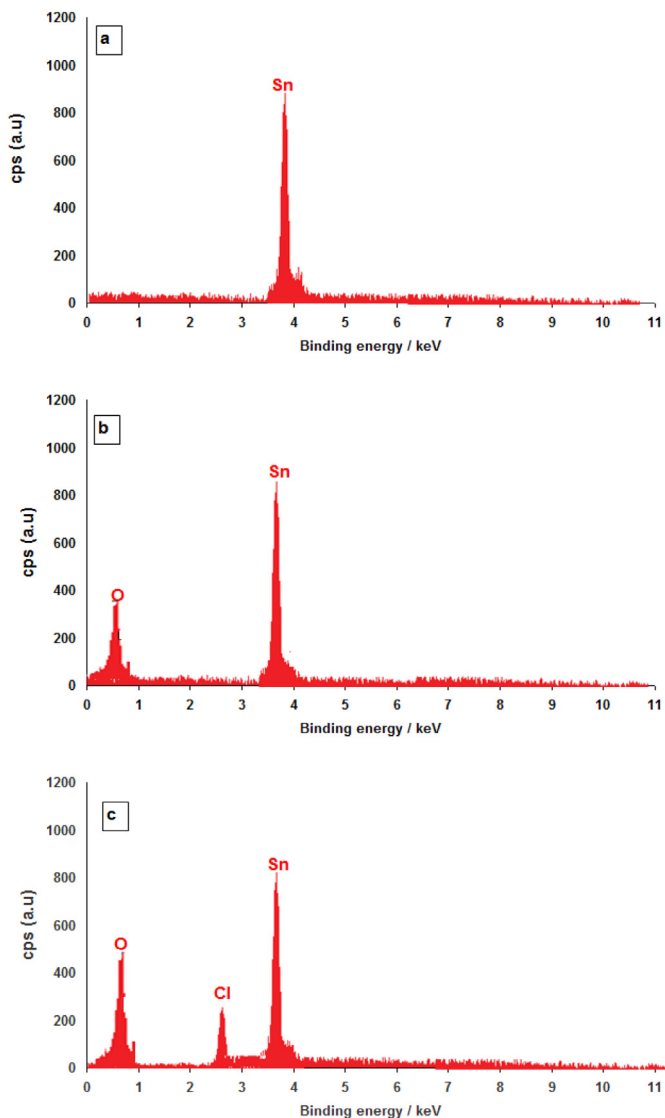
Fig. 9. EDX survey spectra recorded for tin electrode (a) before exposure to the acidic medium, (b) after immersion in 1.0 M lactic acid solution and (c) after immersion in 1.0 M lactic acid solution containing 0.5 M sodium perchlorate.

(Fig. 8c), rougher surfaces with pits were observed showing the damage caused by sodium perchlorate.

EDX analysis of tin electrode in 1.0 M lactic acid solution in the absence and presence of 0.5 M of sodium perchlorate at 25 °C are presented in Fig. 9. Before being exposed to the aggressive medium (Blank), The EDX survey spectra presented in Fig. 9a showed the characteristic peak of the element constituting the polished tin surface (Sn). Fig. 9b shows the EDX spectra view of surface sample after being exposed to 1.0 M lactic acid solution in the absence of sodium perchlorate. It clears that two main signals are easily noticed due to the presence of oxygen and Sn. This indicates that tin oxides are formed as corrosion products on the metal surface. In the presence of 0.5 M of sodium perchlorate in 1.0 M lactic acid solution (Fig. 9c), Cl signal was observed on the tin surface, in addition, O signal is significantly enhanced due to the oxygen atoms of the ClO_4^-. This reflects the strong adsorption of ClO_4^- ions on the oxide surface.

Therefore, the EDX and SEM examinations of the tin surface support the results obtained from the chemical and electro-chemical methods.

4. Conclusion

Production of hydrogen has been achieved using the reaction of tin with lactic acid solution. This process could abate production costs relative to processes based on hydrolysis of chemical hydrides as raw materials for in situ hydrogen generation. It has been shown how hydrogen production rate can be regulated varying experimental parameters such as the concentration of lactic acid, the temperature and the addition of sodium perchlorate. The prevention of tin surface passivation using sodium perchlorate in lactic acid, showing that sodium perchlorate can be a suitable promoting agent to hydrogen generation. The rise of temperature aids sodium perchlorate in producing localized pitting and rupture of the passive layer on tin metal.

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